Prototype of the gas chromatograph – mass spectrometer to investigate volatile species in the lunar soil for the Luna-Resurs mission.

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Abstract

In preparation for the Russian Luna-Glob and Luna-Resurs missions we combined our compact time-of-flight mass spectrometer (TOF-MS) with a chemical pre-separation of the species by gas chromatography (GC). Combined measurements with both instruments were successfully performed with the laboratory prototype of the mass spectrometer and a flight-like gas chromatograph. The system was tested both with a mix of hydrocarbons and a mixture of noble gases. Due to its capability to record mass spectra over the full mass range at once with high sensitivity and a dynamic range of up to 10^6 within 1s, the TOF-MS system is a valuable extension of the GC analysis. The combined GC-MS complex is able to detect concentrations of volatile species in the soil sample of about $2 \cdot 10^{-9}$ by mass.

1 Introduction

To investigate the lunar poles, the Russian Space Agency, Roskosmos, will launch the two spacecraft Luna-Glob and Luna-Resurs landing on these poles in 2015 and 2019, respectively. Since all lunar soil samples available on Earth originate from a restricted area at the lunar near side, close to the equator, the investigation of the lunar poles is of interest for extending understanding of the Moon's composition and history.

The detection and analysis of the volatile species in the lunar soil sample will be performed by a gas-chromatography mass spectrometer complex, the GC-MS analytic complex. As a part of this experiment our Neutral Gas Mass Spectrometer (NGMS) was selected to detect and analyse the volatile species in the lunar soil. The NGMS is a time-of-flight type mass spectrometer (TOF-MS) with a grid-less ion mirror (reflectron) integrated in the ion path to enhance mass spectrometric performance [Scherer et al., 2006]. The ions are generated out of the neutral gas by electron impact ionisation. The ion optical design of NGMS is based on the P-BACE instrument [Abplanalp et al., 2009]. A detailed description of the instrument currently under development for the lunar missions can be found in [Wurz et al., 2012].

With NGMS, as a TOF-MS, complete mass spectra are recorded at once without the necessity of scanning over the desired mass range. The high cadence of recorded mass spectra allows the accumulation of mass spectra with a large dynamic range of up to 10^6 within 1s integration time. These qualities together with the high sensitivity are needed for the analysis of the gas at the output of a gas chromatographic column (GC), which provides temporal pre-separation of the sample.

An additional feature of NGMS is that it can be operated as a standalone instrument for sampling the tenuous lunar exosphere.

2 Experimental

2.1 GC-MS Setup

The prototype of NGMS is the refurbished mass spectrometer of the P-BACE mission. On the one hand this mass spectrometer was modified to allow an interface with a gas chromatographic column and on the other hand same elements of the ion optics were replaced with prototype parts of the flight design for NGMS. To get significant measurements with the GC-MS prototype, spare units of the gas chromatographic instrument from the Phobos-Grunt mission were used. Available are two GC modules of identical build, one assembled with an MXT-5 chromatographic column for separation of hydrocarbons and one populated with a Carbobond column for noble gas separation. Both modules are equipped with a Thermal Conductivity Detector (TCD).

For sampling reasons a sample loop with a defined volume is filled with the calibration gas mixture. The sample volume in the loop is then injected by the use of a standard sample valve (cf. Figure 1). The injected sample is carried by helium as carrier gas through the gas chromatographic column. In this 30 m of capillary column the gas mix in the sample is separated based on the different retention times of the different species. At columns output the gas is guided through a short piece of standard 1/32” stainless steel capillary to the gas inlet interfacing the GC with the NGMS. Since only a fraction of the GC gas can be introduced into the mass spectrometer due to pressure reasons, this gas inlet consists of a flow splitter with an approximately 30 µm hole in diameter. Safe operation of NGMS is guaranteed by the pressure reduction of the flow splitter while using as much as possible of the GC gas to be as sensitive as possible. The rest of the GC gas leaves the GC-MS instrument through the exhaust, which is simulated in the prototype by a roughing vacuum pump. The delicate hole in the gas inlet is protected against dust by two frit-filters, each one at entrance and exit capillary.

There is a certain pressure needed in the capillary to provide good flow conditions for sample transportation until the sample reaches the gas inlet of NGMS. Since the output capillary is connected to vacuum a pressure gauge is installed in the capillary line for monitoring and characterising this pressure in the prototype setup (see Figure 1).

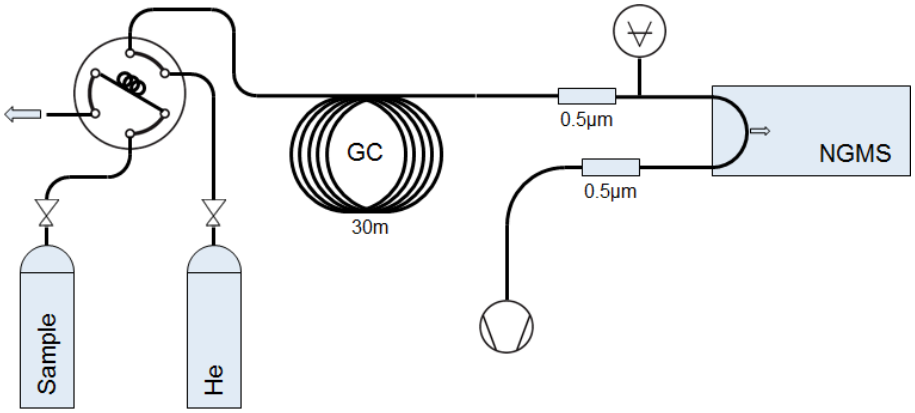
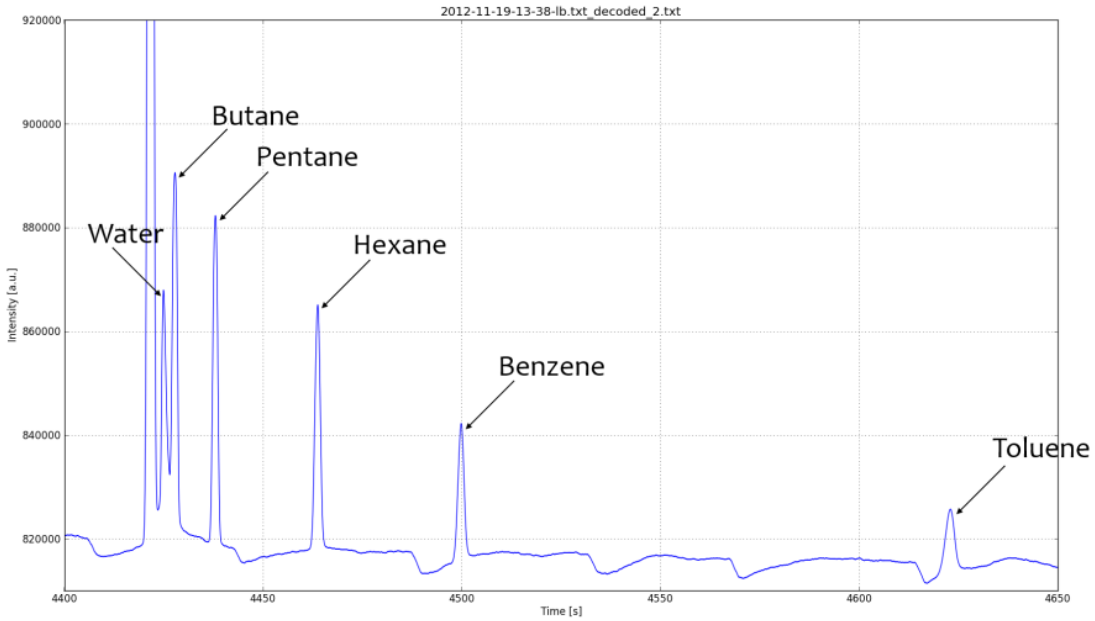


Figure 1: Scheme of the laboratory GC-MS setup with sample gas (sample), He carrier gas (He), sample valve (SV), gas chromatographic column (GC), frit-filters, pressure gauge (PG), and NGMS inlet.

2.2 Measurements

2.2.1 GC-MS analysis of hydrocarbons

The very first measurements with the lunar GC-MS prototype were performed with the MXT-5 chromatographic module using a relatively large sample with a 250 µl sample loop. The first calibration sample was a gas mixture of mostly He with a variety of hydrocarbons at 1000 ppm concentration each: CO_2, n-butane, n-pentane, n-hexane, benzene and toluene. After sample injection into the GC column NGMS recorded one mass spectrum after the other, each with 1s integration time at 10 kHz extraction frequency. This means each spectrum is a histogram of 10^4 single measurements.



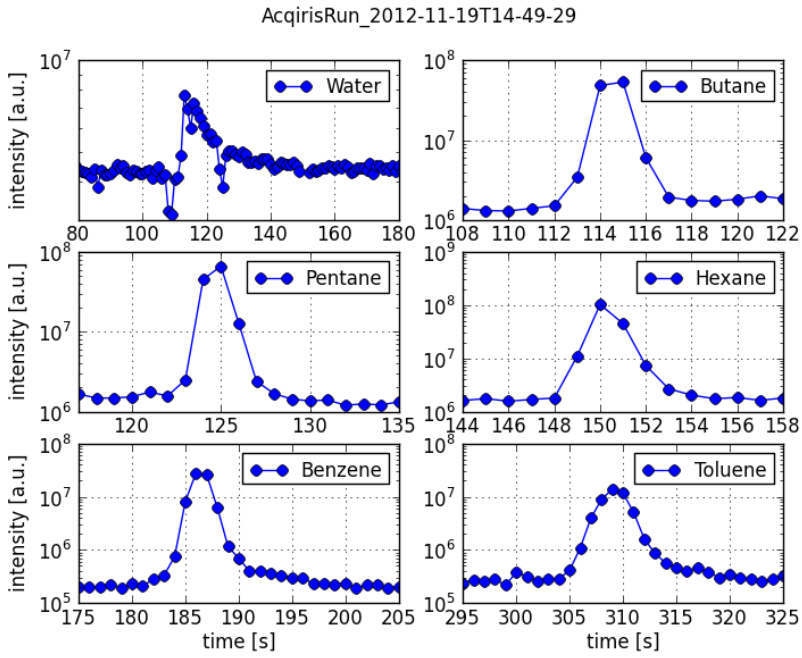


Figure 2: TCD data of a hydrocarbon mix (top) and mass spectrometric analysis of the peaks at GC output by NGMS (bottom).

The top panel of Figure 2 shows TCD data over the full retention time span, where the hydrocarbons are well separated. Start of the chromatogram is at XXXX, where the large peak occurs, a feature of the TCD ??? A water peak is also indicated in this chromatogram, but its identification was only possible with the help of the mass spectrometer, as explained below. CO_2 ???

The lower panel shows mass spectrometric analysis of the GC peaks with NGMS. Since these organic compounds are partially destroyed during analysis due to electron impact ionization, several peaks of one compound are available in each mass spectrum. By selecting the most favourable fragments of each compound the signal-to-noise ratio can be maximised as it is done in Figure 2. Using the same composite signal gives the signal-to-noise values in Table 1 for each GC peak visible on TCD (cf. top panel in Figure 2). Beside the possibility to increase signal-to-noise the fragments can be used to identify the measured species, since the fragmentation pattern is characteristic to the molecular structure.

Table 1: Retention times and signal-to-noise ratios for each GC peak during the first GC-MS measurement using the MXT-5 GC module for hydrocarbon separation at a column temperature of 40°C and 2.3ml/min helium flow in combination with a 250 µl sample loop.

Event	c [ppm]	t_ret [s]	S/N (NGMS)	S/N (TCD)	FWHM (NGMS) [s]	FWHM (TCD) [s]
CO_2	1000	92.0	358	317	1.4	1.4
H_2O	?	95.4	32	36	7.0	1.6
Butane	1000	98.1	863	51	1.5	1.5
Pentane	1000	108.3	1037	45	1.5	1.5
Hexane	1000	134.0	2494	34	1.1	1.7
Benzene	1000	170.1	818	20	2.0	1.9
Toluene	1000	293.2	518	9	2.8	2.8

According to the retention times determined from these measurements, Table 1 shows clearly that with a helium flow of 2.3 ml/min and a column temperature of only 40°C a good separation of all the hydrocarbon compounds can be achieved and that one single GC-MS analysis with the available organic compounds needs approximately 5 min. The measurements also show the value of having NGMS at the columns output, since the achievable signal-to-noise ratio of a GC peak measured with NGMS is a few decades better than with TCD alone. The best example for this is Toluene. Due to the longest retention time Toluene spends the longest time in the column and gets therefore a broader peak shape with smaller amplitude. This leads to a very low signal-to-noise ratio on TCD while the signal-to-noise value of NGMS is still very good.

The big advantage of GC-MS coupling is that also species can be detected on a mass line where relatively large background is present. An evidence for this is the water peak in Figure 2. Initially it was unknown to which compound the corresponding peak in TCD data was belonging, but the analysis of the mass spectra recorded with NGMS showed clear features on the mass lines belonging to water. With the help of NGMS it was possible to identify the chemical nature of the unknown GC peak, although there is large background on these mass lines, since the water group and especially the water peak itself are very prominent in residual gas mass spectra of this prototype instrument. The origin of this water GC peak has to be searched in the sampling system. While no measurements are performed the output of the sample loop is at air pressure and therefore also exposed to the water in the air. Even if the sample loop is purged before injecting the volume of the sample loop to the column it is very likely that the calibration gas mixture is contaminated by a small portion of water.

The values for the peak width in time (full width at half maximum) presented in Table 1 show that the short transfer line between the GC output and the gas inlet to NGMS do not affect the peak shape much for most of the peaks, except for water, where the peak shape is much broader in the mass spectrometer than measured with TCD. Generally it seems the peaks are slightly broader measured with NGMS, but this might be also because mass spectra were accumulated for 1 second each: More data points per GC peak would help to detect the peak shape better. As it will be shown in the next chapter, this can be done easily with NGMS.

Different measurements with this column showed that even with a smaller sample loop of only 25 µl (instead of 250 µl) and a decade less concentrated calibration gas mixture (only 100 ppm of the same components as described above) NGMS is able to detect clear features of all the species without any problem.

To derive a detection limit for the prototype of the GC-MS system, it can be assumed that NGMS is able to detect gas concentrations that are again one decade lower based on our measurements presented in Table/Figure ….. Further assuming a mean molar mass of 2.2 g for moon's regolith [Wurz et al., 2007] and a typical oven volume of 52 mm^3 [Alex Sagpir fragen], a detection limit of about $2 \cdot 10^{-9}$ by mass can be calculated for the GC-MS prototype setup. For comparison, for the SAM instrument on the Curiosity rover a sensitivity for organic compounds of 1 – 10 ppb by mass has been quoted [Mahaffy et al., 2012].

2.2.2 GC-MS analysis of noble gases

The first measurements with the Carbobond GC module were again done with a 250 µl sample loop and a noble gas mix containing each 1000 ppm of neon, krypton and xenon in pure helium. Typically

NGMS recorded continuous mass spectra of the GC gas with 1 s integration time and 10 kHz extraction frequency (Figure 3). Table 2 shows the resulting values of these measurements.

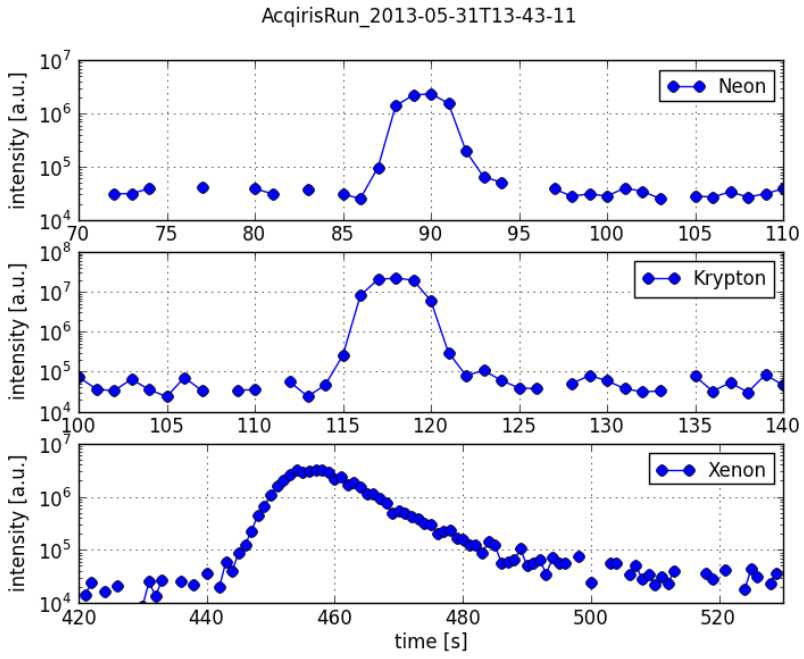


Figure 3: Mass spectrometric analysis of the peaks at GC output by NGMS for the noble gas mix.

Table 2: Retention times and signal-to-noise ratios for each GC peak during the first GC-MS measurement using the Carbobond GC module for noble gas separation at a column temperature of 40°C and 2.3ml/min helium flow in combination with a 250 µl sample loop.

Event	c [ppm]	t_ret [s]	S/N (NGMS)	S/N (TCD)	FWHM (NGMS) [s]	FWHM (TCD) [s]
Neon	1000	74.5	487	12	3.2	3.5
Krypton	1000	101.4	1217	24	3.2	3.5
Xenon	1000	424.6	593	8	12.1	11.7

With the same operation parameters as used for the MXT-5 column (40°C column temperature, 2.3 ml/min helium flow) a separation of all components out of the gas mix is achievable. Again NGMS is able to detect the species with a much better signal-to-noise ratio than the TCD does. Conspicuous is the very long retention time of xenon, which leads to a smeared GC peak with small amplitude (c.f. Figure 3), similar to toluene in the hydrocarbon analysis (Table 1). Due to this behaviour the signal-to-noise ratio is smaller and the peak is nearly at the TCD detection limit, despite the relatively large sample.

This non-optimal GC operation shows also that NGMS is able to detect species without any problems at conditions where a TCD fails. Since the calculated signal-to-noise ratios for the noble gases are in the same range as for the hydrocarbons and the same setup was used it can be estimated that the detection limit is also in the same range of about $2 \cdot 10^{-9}$ by mass for our GC-MS prototype.

By increasing the column temperature from 40°C to 80°C the situation for xenon can be improved: The retention time of xenon is nearly 5 min shorter and the signal-to-noise ratio can be improved due to a narrower and therefore larger GC peak. While xenon needs with the higher column temperature nearly 5 min less time to pass the chromatographic column, the retention times of the remaining noble gases are shortened only by a few seconds.

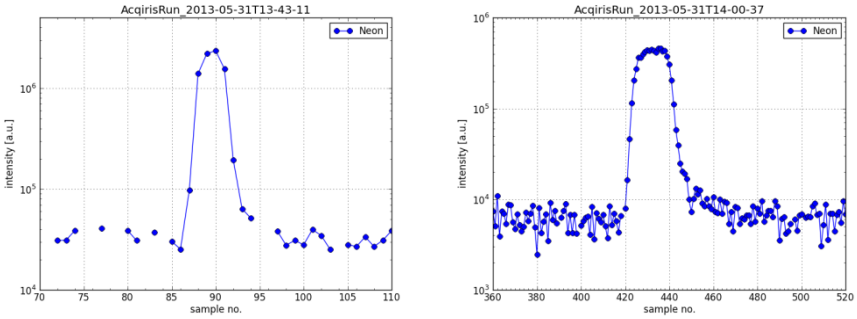


Figure 4: Comparison between sampling of a GC peak with 1 s (left panel) and 200 ms (right panel) integration time per mass spectrum.

Depending on the width of a GC peak the typical continuous acquisition of mass spectra with 1s integration time might not lead to an optimal sampling of the peak shape. This problem can be avoided by changing the integration time of a single mass spectrum. With NGMS the integration time per spectrum can be chosen in GC mode between 100ms and up to 1s. Figure 4 shows a comparison between two different sampling rates. In both cases the sample was injected under identical conditions with the only difference of the sampling rate of NGMS. The left panel shows the neon peak sampled with 1s mass spectra while the right panel shows the same peak sampled with 200ms mass spectra. These integration times correspond with an extraction frequency of 10kHz to a histogram of 10000 respectively 2000 extractions per data point. Naturally the signal-to-noise value decreases with shorter integration times why the highest possible sampling rate is not necessarily the best choice.

3 Conclusion

Coupled measurements with chemical pre-separation of the gaseous sample by gas chromatography and subsequent analysis by our time-of-flight type neutral gas mass spectrometer NGMS were performed successfully. Both a mix of hydrocarbons and a noble gas mixture were tested successfully.

While a GC-MS measurement is running, NGMS is able to record continuously mass spectra over the full mass rage of the GC output to record the maximum possible chemical information from the sample. In GC-MS mode the integration time per mass spectrum and therewith the sampling frequency of the GC output by NGMS can be chosen between 100ms and 1s. Due to the high sensitivity and the large dynamic range of up to 10^6, we can detect about 2ppb by mass with the prototype setup of the GC-MS instrument. For comparison, a sensitivity of 1 – 10ppb for organic compounds has been quoted for the SAM instrument on the Curiosity rover [Mahaffy2012].

Due to the successful measurements with the NGMS prototype the development of the flight design for NGMS was accomplished and currently the manufacturing of flight hardware is in progress to be ready for flying to the moon.

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